

[JP,05-341521,A(1993)]

Japanese (PDF)

File Wrapper Information

FULL CONTENTS CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART
EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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Notes:

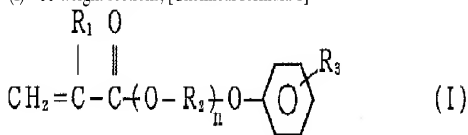
1. Untranslatable words are replaced with asterisks (***)
2. Texts in the figures are not translated and shown as it is

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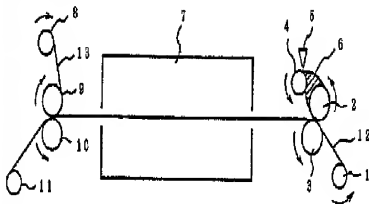
Dictionary: Last updated 03/12/2010 / Priority: 1. Chemistry / 2. Technical term / 3. Natural sciences

FULL CONTENTS**[Claim(s)]**

[Claim 1](A) The polyethylene glycol structure content monomer 5 shown by (a) general formula (I) - 60 weight sections, [Chemical formula 1]

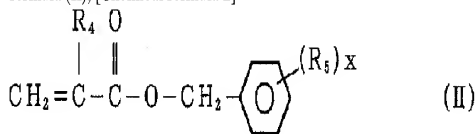


(R₁ expresses hydrogen, halogen, or a methyl group among a formula, R₂ expresses ethylene or a propylene group, R₃ expresses an alkyl group which has a hydrogen atom and the numbers of carbon atoms 1-9, and n is an integer of 1-23)

Drawing selection **Drawing 1**

[Translation done.]

(b) Zero to vinyl monomer 60 weight section containing the aromatic ring shown by general formula (II), [Chemical formula 2]



(R₄ expresses hydrogen, halogen, or a methyl group among a formula, R₅ expresses the alkoxy group or halogen atom which has an alkyl group which has the numbers of carbon atoms 1-3, or the numbers of carbon atoms 1-3, and x is an integer of 0-5)

(c) 30 to vinyl monomer 40 weight section and (d) above (a) which have a carboxyl group, Vinyl monomers 0 other than the (c) component - 20 weight sections (b) And (a), [the high molecular compound produced by the total amount of (b), (c), and the (d) component making copolymerize in the quantity used as 100 weight sections] [the compound which carries out the piece owner of an oxirane ring and the ethylenic unsaturated bond, respectively] The unsaturated high molecular compound produced by making react so that an epoxy group equivalent / carboxyl group equivalent ratio may serve as the range of 0.2-0.6, (B), [at least one sort of novolak type epoxy resin and unsaturated carboxylic acid which are chosen from the group which consists of orthocresol novolak type epoxy resin, phenol novolak type epoxy resin, and halogenated-phenols novolak type epoxy resin] The acid anhydride denaturation epoxyacrylate compound produced by making a saturation or unsaturated polybasic acid anhydride react to the unsaturated compound produced by making react so that an acid equivalent / weight per epoxy equivalent ratio may become the range of 0.5-1.05, (C) The photosensitive resin composition containing the photoinitiator which generates a free radical by the exposure of the photopolymerization nature unsaturated compound and (D) active light which have at least two ethylene at the end.

[Claim 2](A) the photopolymerization nature unsaturated compound 5 - 30 weight sections (however, (A).) which have at least two ethylene at the unsaturated high molecular compound 20 - the 50 weight-section (B) acid anhydride denaturation epoxyacrylate compound 20 - the 75 weight section (C) end (B) And the photosensitive resin composition containing the photoinitiator 0.01 which generates a free radical by the exposure of (D) active light and it makes a total amount of (C) into 100 weight sections - 20 weight sections (correcting and receiving total amount 100 weight section of (A), (B), and (C)) according to claim 1.

[Claim 3]A photosensitive element which has a base film which supports a layer and this layer of the photosensitive resin composition according to claim 1 or 2.

[Claim 4]The photosensitive element according to claim 3 which laminates further a cover film which can exfoliate on a layer of a photosensitive resin composition.

[Claim 5]A manufacturing method of a metal-plating resist which applies a solution of the photosensitive resin composition according to claim 1 or 2 on a substrate, and performs exposure occasion development in image after desiccation.

[Claim 6]A manufacturing method of a metal-plating resist which laminates a layer of the photosensitive resin composition to a substrate, and performs exposure occasion development in image using the photosensitive element according to claim 3 or 4.

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the manufacturing method of a photosensitive resin composition, the photosensitive element which used this, and a metal-plating resist. It is related with the manufacturing method of the photosensitive element which consists of a base film which supports in detail the layer and this layer of the alkaline development type photosensitive resin composition which has outstanding characteristics and this constituent which can be used as a resist for nonelectrolytic plating in the case of manufacture of a printed wiring board etc., and a metal-plating resist.

[0002]

[Description of the Prior Art]Conventionally, manufacture of the printed wiring board is mainly performed by the subtractive process which uses together non-***** attachment metal plating and electrolysis metal plating, forms a through hole conduction part, and forms a wiring pattern part by etching. On the other hand, the additive process which forms a through hole conduction part and a wiring pattern part by nonelectrolytic plating is put in practical use, and since it is suitable for detailed wiring or a byway through hole, it is observed as a future high-density printed wiring board manufacturing method.

[0003]In this additive process, high alkalinity (usually pHs 11-13.5), The resist for nonelectrolytic plating borne for a long time (usually 4 to 50 hours) is required for the electroless plating liquid of high temperature (usually 60-80 **), and in order to form 150 micrometers (line width and interval) detailed wiring, it is difficult and the resist for screen-stencil usually requires photoresist.

[0004]The proposal of the photoresist for additive processes is made by JP,S50-43468,A, JP,S54-770,A, JP,S58-100490,A, JP,S58-199341,A, JP,S59-12434,A, JP,S60-101532,A, etc. There is little contamination of a non-electrolytic copper plating solution, and the photoresist excellent in mass production nature is made by JP,S63-18692,A. However, each of such proposed photoresist uses organic solvents, such as 1,1,1-trichloroethane, for the developer.

There was a problem in respect of work environment or a cleanup cost.

There is use of a halogen system organic solvent in the direction regulated from the problem of the latest environmental pollution, and the photoresist in which development is possible was called for by the alkaline aqueous solution also with the additive process.

[0005]By an alkaline aqueous solution, as photoresist for nonelectrolytic plating in which development is possible, [JP,H2-166452,A] The alkaline development type resin composition

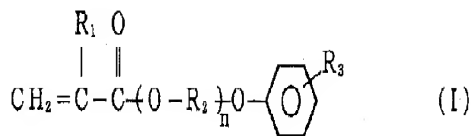
which contains collectively the compound which made hydroxy alkylene (meta) acrylate add to the copolymer of maleic anhydride and the aromatic hydrocarbon which has a vinyl group, and the epoxy acrylate of carboxy group content is indicated. Since flexibility was low, when a crack occurred, or it used as a photosensitive element on the occasion of radio solution coppering and the cutter etc. cut the metal-plating resist formed using this resin composition although it was excellent in film hardness, it had problems, like the photosensitive layer of the circumference of a cut section scatters.

[0006]The development by an alkaline aqueous solution is possible, and the photopolymerization hardening constituent using the polymer which has polyethylene glycol whose end group is a phenoxy group in a side chain is indicated by JP, S62-153308, A as photoresist which has resistance in alkali etchant. Although the metal-plating resist formed using this resin composition shows comparatively good resistance at an alkali etching process (pH eight to 9 temperature of 50 **, 1 to 3 minutes as an example), [a resist] In pH 12.3 temperature of 72 **, and 24hr), a part of metal-plating resist exfoliated with time as a (example, or the plating solution was polluted as non-electrolytic copper galvanizer, and it had the problem that a copper deposition rate became slow.

[0007]JP, H2-230154, A has disclosed the photopolymerization nature constituent which contains collectively styrene, the polymer represented by the compound which added glycidyl methacrylate to the 2 yuan copolymer of mono-maleate iso-propyl, and the polymer represented by benzyl methacrylate, methacrylic acid-2-hydroxy butyl, and the 3 yuan copolymer of methacrylic acid by an alkaline aqueous solution as a copper metal-plating resist material in which development is possible. Although the metal-plating resist formed using this resin composition showed comparatively good substrate adhesion, in a non-electrolytic copper metal-plating process, there was a problem on which a part of metal-plating resist exfoliates.

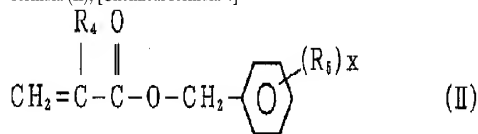
[0008]
[Problem to be solved by the invention]This invention solves the problem of the above-mentioned conventional technology, and, [the purpose] Have the good development nature by an alkaline aqueous solution, and it excels in light sensitivity, resolution, and metal-plating-proof nature, In there being no abnormal precipitation and plating solution contamination of metal-plating copper and using as a permanent resist, electric insulation, The manufacturing method of the photosensitive element which consists of a base film which supports the layer and this layer of a photosensitive resin composition suitable as photoresist excellent in electrolytic corrosion resistance for non-electrolytic copper metal plating and this constituent, and a metal-plating resist is provided.

[0009]
[Means for solving problem](A) The polyethylene glycol structure content monomer 5 shown by (a) general formula (I) - 60 weight sections, [Chemical formula 3]



(R₁ expresses hydrogen, halogen, or a methyl group among a formula, R₂ expresses ethylene or a propylene group, R₃ expresses the alkyl group which has a hydrogen atom and the numbers of carbon atoms 1-9, and n is an integer of 1-23)

(b) Zero to vinyl monomer 60 weight section containing the aromatic ring shown by general formula (II), [Chemical formula 4]



(R₄ expresses hydrogen, halogen, or a methyl group among a formula, R₅ expresses the alkoxyl group or halogen atom which has an alkyl group which has the numbers of carbon atoms 1-3, or the numbers of carbon atoms 1-3, and x is an integer of 0-5)

(c) 30 to vinyl monomer 40 weight section and (d) above (a) which have a carboxyl group, Vinyl monomers 0 other than the (c) component - 20 weight sections (b) And (a), [the high molecular compound produced by the total amount of (b), (c), and the (d) component making copolymerize in the quantity used as 100 weight sections] [the compound which carries out the piece owner of an oxirane ring and the ethylenic unsaturated bond, respectively] The unsaturated high molecular compound produced by making react so that an epoxy group equivalent / carboxyl group equivalent ratio may serve as the range of 0.2-0.6, (B), [at least one sort of novolak type epoxy resin and unsaturated carboxylic acid which are chosen from the group which consists of orthocresol novolak type epoxy resin, phenol novolak type epoxy resin, and halogenated-phenols novolak type epoxy resin] The acid anhydride denaturation epoxyacrylate compound produced by making a saturation or unsaturated polybasic acid anhydride react to the unsaturated compound produced by making react so that an acid equivalent / weight per epoxy equivalent ratio may become the range of 0.5-1.05, (C) The photosensitive resin composition containing the photoinitiator which generates a free radical by the exposure of the photopolymerization nature unsaturated compound and (D) active light which have at least two ethylene at the end, It is related with the manufacturing method of the photosensitive element which consists of a base film which supports the layer and this layer of this photosensitive resin composition, and a metal-plating resist.

[0010]The photosensitive resin composition which this invention proposes is explained in detail below. The photosensitive resin composition of this invention is an essential ingredient about the

above-mentioned unsaturated high molecular compound. [(A) Component] It contains by carrying out. Such an unsaturated high molecular compound can be easily manufactured by making the compound which carries out the piece owner of an oxirane ring and the ethylenic unsaturated bond, respectively react to the high molecular compound produced by making above-mentioned (a), (b), (c), and (d) component copolymerize.

[0011]As a (a) component shown by general formula (I), n is phenoxyethylene glycol (meta) acrylate of 1-23, for example. [(meta) Acrylate means methacrylate and acrylate. It is] like the following. Alkyl phenoxyethylene glycol (meta) acrylate, phenoxypropylene glycol (meta) acrylate, alkyl phenoxypropylene glycol (meta) acrylate, etc. can be mentioned. As an alkyl group in the case of alkyl phenoxy, a methyl group, an ethyl group, a propyl group, a butyl group, etc. are raised. In the alkyl group in which a carbon number exceeds 9 in R_3 , development

nature is inferior. If n exceeds 23, non-[proof] electrolytic copper metal-plating nature will fall.

[0012][as a (b) component shown by general formula (II)] For example, benzyl methacrylate, methacrylic acid-4-methylbenzyl, Methacrylic acid-3-methylbenzyl, a methacrylic acid-4-benzyl chloride, methacrylic acid-4-methoxybenzyl, methacrylic acid-4-ethylbenzyl, methacrylic acid-4-iso-propylbenzyl, and benzyl acrylate can be mentioned. If a number of carbon atoms exceeds 3 in R_5 , the compatibility at the time of considering it as a resin composition will fall.

[0013](c) Acrylic acid, methacrylic acid, etc. are mentioned as a vinyl monomer which has a carboxyl group which is a component.

[0014][as vinyl monomers (d) other than (a), (b), and (c)] For example, methyl methacrylate, methyl acrylate, ethyl methacrylate, Ethyl acrylate, n-propyl methacrylate, n-propylacrylate, Cyclohexyl methacrylate, cyclohexyl acrylate, butyl methacrylate, butyl acrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl acrylate, etc. can be mentioned, and methyl acrylate and methyl methacrylate are preferred.

[0015]The unsaturated high molecular compound of the (A) component used for this invention is obtained by making it blend and copolymerize so that total of the above (a), (b), (c), and the (d) component may serve as 100 weight sections.

[0016](a) As for the amount of the component used, it is preferred for it to be considered as five to 60 weight section, and to consider it as five to 40 weight section. (a) When a crack occurs that the amount of the component used is less than five weight sections in a metal-plating resist on the occasion of non-electrolytic copper metal plating, or it uses as a photosensitive element and a cutter etc. cut, there are problems, like the photosensitive layer of the circumference of a cut section scatters. If the amount of the (a) component used exceeds 60 weight sections, contamination of non-electrolytic copper metal plating will increase.

[0017](b) Let the amount of the component used be zero to 60 weight section. (b) If the amount of the component used exceeds 60 weight sections, in the case of non-electrolytic copper metal plating, a crack will occur in a metal-plating resist, or alkali development property will fall to it.

[0018](c) Let the amount of the component used be 30 to 40 weight section. (c) If development

nature falls in less than 30 weight sections and the amount of the component used exceeds 40 weight sections, non-[proof] electrolytic copper metal-plating nature will fall.

[0019](d) Let the amount of the component used be zero to 20 weight section. (d) If the amount of the component used exceeds 20 weight sections, all the metal-plating characteristics will fall. [0020]Next, [as a compound which carries out the piece owner of the oxirane ring and ethylenic unsaturated bond which make the above (a), (b), (c), and the (d) component react to the high molecular compound produced by copolymerizing, respectively] For example, metaglycidyl acrylate, glycidyl methacrylate, acrylic glycidyl ether, alpha-ethylacrylic glycidyl, crotonylglycidyl ether, crotonic acid glycidyl, isocrotonic acid glycidyl, etc. are mentioned. The unsaturated high molecular compound of the (A) component is obtained by making said high molecular compound react to these compounds.

[0021]Said high molecular compound Namely, ketones, Cellosolve Solvent, an ether system, Dissolve in inactive organic solvents, such as a nonpolar solvent, and as a catalyst Triethylamine, The third class amine, such as tri-n-butylamine, diethylcyclohexylamine, and a triethylene diamine, It is obtained by adding quarternary ammonium salt, such as benzyltrimethylammonium chloride and benzyl chloride triethyl ammonium, etc., adding hydroquinone, p-methoxy phenol, etc. as polymerization inhibitor further, and making the above-mentioned compound react at 80-110 °C under oxygen existence.

[0022]It is necessary to make a high molecular compound and the compound which carries out the piece owner of an oxirane ring and the ethylenic unsaturated bond, respectively react here so that an epoxy group equivalent / carboxy group equivalent ratio may serve as the range of 0.2-0.6. In less than 0.2 equivalent ratio, non-[proof] electrolytic copper metal-plating nature falls, if equivalent ratio 0.6 is exceeded, during manufacture, gelling will be caused or alkali development property will fall.

[0023]Thus, it is preferred to consider it as 20 - 50 weight section as amount of the obtained (A) component used to total amount 100 weight section of the (A) component, the (B) component, and the (C) component, and it is more preferred to consider it as 25 - 40 weight section. (A) There are exudation from the side by flow of a photosensitive layer when the amount of the component used considers it as a photosensitive element in less than 20 weight sections, and a tendency which spilling generates when a cutter etc. cut. (A) When the amount of the component used exceeds 50 weight sections, there is a tendency for non-[proof] electrolytic copper metal-plating nature to fall.

[0024][the acid anhydride denaturation epoxyacrylate compound which is the (B) component of this invention] [at least one sort of novolak type epoxy resin and unsaturated carboxylic acid which are chosen from the group which consists of orthocresol novolak type epoxy resin, phenol novolak type epoxy resin, and halogenated-phenols novolak type epoxy resin] It is obtained by making a saturation or unsaturated polybasic acid anhydride react to the unsaturated compound produced by making carry out an addition reaction so that an acid equivalent / weight per epoxy equivalent ratio may become the range of 0.5-1.05.

[0025]The above-mentioned unsaturated compound has two class hydroxyl groups, and when an acid equivalent/weight per epoxy equivalent is less than one, it has an epoxy group with two class hydroxyl groups.

[0026][the novolak type epoxy resin used for this invention] For example, it is obtained by making epichlorohydrin react to phenolic hydroxyl of the novolak type resin produced by making aldehyde react to orthocresol, phenol, halogenated phenols, etc. under existence of an acid catalyst under existence of an alkali, and is commercially available.

[0027][as orthocresol novolak type epoxy resin] For example, the Ciba-Geigy make, Araldite ECN1299 () [99 ** of softening temperatures] The weight per epoxy equivalent 230, ECN1280 (80 ** of softening temperatures, weight per epoxy equivalent 230), ECN1273 (73 ** of softening temperatures, weight per epoxy equivalent 230), the Nippon Kayaku Co., Ltd. make, EOCN104 (90-100 ** of softening temperatures, weight per epoxy equivalents 225-245), EOCN103 (80-90 ** of softening temperatures, weight per epoxy equivalents 215-235), EOCN102 (70-80 ** of softening temperatures, weight per epoxy equivalents 215-235), EOCN101 (65-69 ** of softening temperatures, weight per epoxy equivalents 205-225), etc. are mentioned.

[0028][as phenol novolak type epoxy resin] For example, shell company make, Epicoat 152 (weight per epoxy equivalent 175), Epicoat 154 (weight per epoxy equivalents 176-181), The Dow Chemical Co. make, DEN431 (weight per epoxy equivalents 172-179), DEN438 (weight per epoxy equivalents 175-182), the Tohto Kasei Co., Ltd. make, YDPN-638 (weight per epoxy equivalents 170-190), YDPN-601 (weight per epoxy equivalents 180-220), YDPN-602 (weight per epoxy equivalents 180-220), EPPN201 by Nippon Kayaku Co., Ltd. (weight per epoxy equivalents 180-200), etc. are mentioned.

[0029]As halogenated-phenols novolak type epoxy resin, bromination phenol novolak type epoxy resin, such as the Nippon Kayaku Co., Ltd. make and BREN (the weight per epoxy equivalents 270-300, 35 to 37% of bromine content, 80-90 ** of softening temperatures), etc. are mentioned, for example. As unsaturated carboxylic acid, acrylic acid, methacrylic acid, beta-furil acrylic acid, beta-styryl acrylic acid, alpha-cyano cinnamic acid, cinnamic acid, etc. are used.

[0030]In this invention, the addition reaction of these novolak type epoxy resin and unsaturated carboxylic acid is performed by a conventional method considering an acid equivalent / weight per epoxy equivalent ratio as a range of 0.5-1.05. Since the unsaturated carvone acidity of isolation increases when non-[proof] electrolytic copper metal-plating nature falls [an acid equivalent / weight per epoxy equivalent ratio] by less than 0.5 and an acid equivalent / weight per epoxy equivalent ratio exceeds 1.05, a skin stimulus etc. give on safe the result which is not preferred. [the addition reaction thing (unsaturated compound) of novolak type epoxy resin and unsaturated carboxylic acid] Said novolak type epoxy resin For example, methyl ethyl ketone, methyl-cellosolve acetate, It dissolves in inactive organic solvents, such as ethylcellosolve acetate and cyclohexanone, As a catalyst, the third class amine, such as triethylamine, tri-n-butylamine, and diethylcyclohexylamine, [quarternary ammonium salt such as benzyltrimethylammonium

chloride and benzyl chloride triethyl ammonium, etc.] It is obtained by carrying out a churning reaction in the range of said unsaturated carboxylic acid and the above-mentioned equivalent ratio at 70-110 **, using hydroquinone, p-methoxy phenol, etc. as polymerization inhibitor.

[0031] as a saturation or unsaturated polybasic acid anhydride used in this invention] For example, phthalic anhydride, an anhydrous tetrahydrophthalic acid, anhydrous hexahydrophthalic acid, An anhydrous methyl tetrahydrophthalic acid, an anhydrous methyl 2 substitution butenyl tetrahydrophthalic acid, Itaconic acid anhydride, succinic anhydride, anhydrous citraconic acid, an anhydrous alkenyl acid, The Reno Reign acid addition product of anhydrous dodecenyl succinic acid, anhydrous tricarballic acid, maleic anhydride, and maleic anhydride, an anhydrous KUOREN Dick acid, the maleic anhydride addition product of methylecyclopentadiene, anhydrous alkylation, an alkylene tetrahydrophthalic acid, etc. can be mentioned.

[0032] In this invention, although the addition reaction of these polybasic acid anhydrides and said unsaturated compounds is performed by a conventional method, it is preferred that an acid equivalent / hydroxyl equivalent ratio makes 0.6-2.0 the range from a point of the development nature by an alkaline aqueous solution and the resistance to swelling of a photo-setting film.

When said unsaturated compound has an epoxy group, Since the carboxyl group concentration of the oligomer obtained by the addition reaction of the carboxyl group and epoxy group which are generated by the addition reaction to two class hydroxyl groups of a polybasic acid anhydride occurring falls, it is desirable to pre-increase the amount of the polybasic acid anhydride used as a part for the fall is balanced.

[0033] Especially, [as a desirable acid anhydride denaturation epoxyacrylate compound] Phenol novolak type epoxy resin / acrylic acid / anhydrous tetrahydrophthalic acid (acid equivalent / weight per epoxy equivalent ratio =0.5-1.05, acid equivalent / water acid equivalent ratio =0.6-2.0) system acid anhydride denaturation epoxy acrylate, Cresol novolak type epoxy resin / acrylic acid / anhydrous tetrahydrophthalic acid (acid equivalent / weight per epoxy equivalent ratio =0.5-1.05, acid equivalent / hydroxyl equivalent ratio =0.6-2.0) system acid anhydride denaturation epoxy acrylate can be mentioned.

[0034] (B) As for the amount of the component used, it is preferred to consider it as 20 - 75 weight section to 100 copies of total amounts of the (A) component, the (B) component, and the (C) component, and it is more preferred to consider it as 25 - 60 weight section. (B) When the amount of the component used uses it as a metal-plating resist in less than 20 weight sections, non-[proof] electrolytic copper metal-plating nature falls, and there is a tendency which peeling of a resist produces in a non-electrolytic copper metal-plating process. On the other hand, when the amount used exceeded 75 weight sections and it is considered as a photosensitive element, and a cutter etc. cut, there is a tendency which spilling generates.

[0035] As a (C) component which is a photopolymerization nature unsaturated compound which constitutes the photosensitive resin composition of this invention, all the things known as a photopolymerization nature polyfunctional monomer can be used conventionally. For example, the compound produced by making alpha and beta-unsaturated carboxylic acid react to a

polyhydric alcohol, For example, poly ethylene glycol di(meth)acrylate (the number of ethylene is a thing of 2-14), Bird methylol pro pansy (meta) acrylate, trimethylolpropane bird (meta) acrylate, Trimethylolpropanethoxy bird (meta) acrylate, trimethylolpropanepropoxy bird (meta) acrylate, Tetramethylolmethane bird (meta) acrylate, tetramethylolmethanetetra (meta) acrylate, Poly propyleneglycol di(meth) acrylate (the number of propylene groups is a thing of 2-14), Dipentaerythritol penta (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc., Bisphenol A polio KISHIECHI range (meta) acrylate. For example, bisphenol A dioxy ECHIRENJI (meta) acrylate, the compound produced by bisphenol A trio KISHIECHI range (meta-) acrylate, bisphenol A deca OKISHIECHI range (meta-) acrylate, etc. adding alpha and beta-unsaturated carboxylic acid to a glycidyl group content compound -- for example, Trimethylolpropane-triglycidyl-ether bird acrylate, Polyvalent carboxylic acid, such as bisphenol A diglycidyl ether diacrylate, For example, the substance which has phthalic anhydride, etc. a hydroxyl group, and an ethylenic unsaturated group, For example, esterification material with beta-hydroxyethyl (meta) acrylate etc., The alkyl ester of acrylic acid or methacrylic acid, for example, acrylic acid (meta) methyl ester, (Meta) Acrylic acid ethyl ester, acrylic acid (meta) butylester, (Meta) 2-ethylhexyl acrylate ester, Tolyene diisocyanate and 2-hydroxyethyl. (Meta) Urethane (meta) acrylate, such as a reactant with acrylic ester and a reactant of trimethyl hexamethylene diisocyanate, cyclohexane dimethanol, and 2-hydroxyethyl (meta) acrylic ester, etc. can be mentioned, Bisphenol A polyoxyethylene dimethacrylate is preferred. These compounds are independent, or can be used together two or more sorts, and can be used.

[0036](C) As for the amount of the component used, it is preferred to consider it as 5 - 30 weight section to 100 copies of total amounts of the (A) component, the (B) component, and the (C) component, and it is more preferred to consider it as 10 - 20 weight section. (C) When there is a tendency for sensitivity to fall [the amount of the component used] by less than five weight sections, and 30 weight sections were exceeded, and a photosensitive element is carried out and it uses, there is a tendency which exudation from the side by flow of a photosensitive layer generates.

[0037][as a photoinitiator of the (D) component which constitutes the photosensitive resin composition of this invention] For example, benzoin methyl ether, benzoin ethyl ether, benzoin isobutyl ether, Benzoin ether, such as benzoin iso-propyl ether and benzoin phenyl ether, Benzophenone, N,N'-tetramethyl 4,4'-diaminobenzophenone (Michler's ketone), Benzophenone, such as N,N'-tetraethyl 4,4'-diaminobenzophenone, Benzyl dimethyl ketal (the Ciba-Geigy make, IRGACURE 651), Benzyl ketals, such as benzyl ethyl ketal, 2,2-dimethoxy- 2-phenyl acetophenone, Acetophenone, such as p-tert-butyl dichloro acetophenone and p-dimethylamino acetophenone, Xanthenes, such as a 2,4-dimethyl thioxan ton and a 2,4-diisopropyl thioxan ton, Hydroxy cyclohexyl phenyl ketone (the Ciba-Geigy make, IRGACURE 184), 1-(4-isopropylphenyl 2-hydroxy-isobutane)-1-ON (the Merck& Co., Inc. make, DAROCUR 1116), 2-hydroxy-2-methyl-1-phenylpropane 1-ON (the Merck& Co., Inc. make, DAROCUR 1173) etc. can be illustrated, these may be used independently, or it may combine and they may be used.

The combination of a 2,4,5-triarylimidazole dimer, 2-mercaptobenzochinac-cortex ZORU, leuco Crystal Violet, tris (4-diethylamine)-2-methylphenyl methane, etc., etc. can also be used.

Although there is no optical start nature at itself, an additive which serves as a better sensitizer system of optical start ability as a whole can be used by using in combination with the substance mentioned above. For example, it is the third class amine, such as triethanolamine to benzophenone, etc.

[0038](D) It is preferred to consider it as 0.01 - 20 weight section as amount of the component used to total amount 100 weight section of the (A) component, the (B) component, and the (C) component, and it is more preferred to consider it as 0.05 - 10 weight section. There is a tendency for sufficient light sensitivity not to be obtained if there is too little this amount used, when too large, the optical absorption in the formed surface increases in the case of exposure, and there is a tendency which becomes insufficient [internal photo-setting].

[0039]The photosensitive resin composition proposed by this invention can contain the secondary component of further others. As a secondary component, it is a thermal-polymerization inhibitor, a color, a pigment, a coating disposition top agent, etc., and these selections are performed to the usual photosensitive resin composition and the thing of the same consideration. It is also possible to contain a small amount of epoxy resins as a secondary component in the range which does not spoil the purpose of this invention.

[0040]As an epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, A bisphenol A type epoxy resin, bisphenol F type epoxy resin, Epoxy resins, such as a bisphenol S-type epoxy resin, a biphenyl type epoxy resin, and cycloaliphatic epoxy resin, Phenyl glycidyl ether, p-butylphenol glycidyl ether, cresyl glycidyl ether, triglycidyl isocyanurate, allyl glycidyl ether, glycidyl methacrylate, etc. are mentioned.

[0041]Next, the photosensitive element which this invention proposes is explained in detail below. The photosensitive element which this invention proposes is obtained by forming the layer of the photosensitive resin composition explained in detail by the above on a base film. Formation of the layer of the photosensitive resin composition to a base film top can be performed with a conventional method. For example, a photosensitive resin composition is uniformly dissolved in organic solvents, such as methyl ethyl ketone, toluene, and a methylene chloride, and this solution is applied by the knife coat method, the roll coat method, etc. on this base film, and it dries and is carried out. As for the amount of residual solvents in a photosensitive layer, it is preferred to press down to 2 or less weight % for characteristics maintenance.

[0042]The heat-resisting property which needs the base film used for this invention at the time of manufacture of a photosensitive element, Although it is preferred to have solvent resistance, mold-release characteristic films, such as a Teflon film and a release paper, are used as a temporary base film, laminating the low film of a heat-resisting property or solvent resistance on this layer, after forming the layer of a photosensitive resin composition besides -- this -- the photosensitive element which exfoliates a temporary base film and has a low base film of a heat-resisting property or solvent resistance can also be manufactured. To active light, the base film may be

transparent or may be opaque. As an example of the base film which can be used, publicly known films, such as a polyester film, a polyimide film, a polyamidoimide film, a polypropylene film, and polystyrene films, can be mentioned.

[0043]When manufacturing a long photosensitive element, this element is rolled round in the shape of a roll in the final stage of manufacture. In this case, it is possible to prevent the transfer attaching to the base film back of the layer of a photosensitive resin composition when it rolls round in the shape of a roll by using the base film which carried out backing using the publicly known method with pressure sensitive adhesive tape etc. It is preferred to laminate the cover film which can exfoliate on the layer of the photosensitive resin composition of this element in order to prevent adhesion of the same purpose and dust.

[0044]As an example of the cover film which can exfoliate, a polyethylene film, a polypropylene film, When there are a Teflon film, paper which carried out the surface treatment, etc. and a cover film is exfoliated, the adhesive strength of the layer of a photosensitive resin composition and a cover film should be just smaller than the adhesive strength of the layer of a photosensitive resin composition, and a base film.

[0045]Although the layer thickness of the photosensitive resin composition which constitutes the photosensitive element of this invention changes with thickness of the metal-plating copper deposited by nonelectrolytic plating, it shall usually be 10-100 micrometers.

[0046]On a substrate, after spreading desiccation or as a photosensitive element, after laminating the layer of the photosensitive resin composition on a substrate, exposure occasion development is performed in image and a metal-plating resist is manufactured by using the photosensitive resin composition in this invention as a solution.

[0047]Next, the example of the directions for the photosensitive element which this invention proposes is explained. Lamination of a up to [the substrate of the photosensitive element which this invention proposes] is easy. That is, as it is, when there is no cover film, when there is a cover film, exfoliating or exfoliating a cover film, the layer of a photosensitive resin composition is carried out the substrate side, and pressurization lamination is heated and carried out. Heating and pressurization lamination can be performed using well-known ordinary pressure laminater by a printed wiring board manufacturer. In the case of a certain thing of unevenness of not less than 10 micrometers, laminating under a reduced pressure or a vacuum is preferred like the printed wiring board with which the conductor wire line was formed for the substrate.

[0048]There are a laminating device etc. which are indicated to JP,S53-31670,B, JP,S55-13341, B, etc. as a device for this. In an additive process, an insulating board is usually used as a substrate. As an insulating substrate, substrates containing a metal core, such as a substrate which formed the epoxy resin insulating layer in both sides, such as laminated sheets, such as paper phenol and glass epoxy, an iron enamel board, and an aluminum board, etc. can be used. These substrates are immersed in the solution which contains a metal-plating catalyst after punching, and can also give a metal-plating catalyst to a through hole inner wall. As such a metal-plating catalyst solution, the Hitachi Chemical Co., Ltd. make, sensitizer HS-101B, etc. can be used. It is

preferred to apply adhesives, in order to make good the adhesion over the substrate of the nonelectrolytic plating copper which makes adhesion of a metal-plating catalyst good on the surface of a substrate and which sake [copper] or deposits.

[0049]As adhesives, what is known can be used as adhesives for additive processes, such as phenol denaturation nitrile rubber adhesive. The epoxy resin shown in JP,S61-276875,A with the point of excelling in electrolytic corrosion and a heat-resisting property, Use of the adhesives which distributed the impalpable powder of the heat resistant resin by which curing treatment was carried out, such as an epoxy resin, polyester resin, and bismaleimide triazine resin, in uncured heat resistant resin, such as epoxy denaturation polyimide resin, polyimide resin, and a phenol resin, is also preferred. By forming detailed unevenness in the surface of the substrate itself, there is also a method of securing the adhesion over the substrate of metal-plating copper, and an adhesive layer in particular is not needed in this case.

[0050]It is a desirable substrate when the laminated sheet which made the inside distribute the compound used as the catalyst of non-electrolytic copper metal plating of Pd compound etc. also deposits nonelectrolytic plating copper to a through hole inner wall. As a substrate in which the adhesive layer include a metal-plating catalyst was formed on the surface of the glass epoxy laminated sheet which included the metal-plating catalyst inside, there is Hitachi Chemical Co., Ltd. make laminated sheet ACL-E-161 grade. When using such a substrate, the process to which a metal-plating catalyst is made to newly adhere becomes unnecessary. In order to make good the adhesion of the nonelectrolytic plating copper which makes adhesion of a metal-plating catalyst good and which sake [copper] or deposits, it is preferred to roughen the adhesive layer surface before nonelectrolytic plating treatment. Although there is the method of immersing in the acidic solution etc. which contain bichromate of soda or chromic acid as the roughening method, if the roughening process of a publicly known passage is a front like non-electrolytic copper galvanizer, it will not matter even if it is after formation of the metal-plating resist pattern described later even if it is before laminating a photosensitive element.

[0051]The exposure after lamination and a development can be performed with a conventional method. That is, when a base film is opaque to active light, after exfoliating a base film, it exposes in image through a negative mask using the light source of a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, etc. Heat-treatment at 50 ** before and behind exposure thru/or 100 ** is preferred in order to improve the adhesion of a substrate and a photosensitive resin layer.

[0052]As a developer used for a development, an alkaline aqueous solution is used, for example, the aqueous solution of the hydroxide of an alkali metal, the aqueous solution of alkali metal phosphate, the aqueous solution of alkali metal carbonate, such as sodium carbonate, etc. are mentioned. Especially the aqueous solution of sodium carbonate is preferred. Preferably, the alkaline development of the resin composition of this invention is 20-40 ** in temperature, and the developer temperature of 10-50 ** can perform it using a commercial developing machine.

[0053]Thus, after forming a metal-plating resist pattern, using the light source of a high-pressure

mercury-vapor lamp, an ultrahigh pressure mercury lamp, etc., re-irradiating with active light is preferred, and the chemical resistance of a metal-plating resist improves.

[0054]It is desirable after the re-exposure of active light to give heat-treatment. By heat-treating, nonelectrolytic plating-proof nature improves remarkably. As cooking temperature and heat time, 140-160 °C and 40 minutes - 90 minutes are mentioned, respectively, for example.

[0055]The solution of the photosensitive resin composition which this invention proposes A dip coating method, By the flow coat method etc., carry out direct coating to a substrate and it is made to be the same as that of the case of the aforementioned photosensitive element after solvent desiccation after laminating a transparent film to active light, such as direct or a polyester film, Through a negative mask, it exposes in image, negatives are developed, and the metal-plating resist which was excellent in characteristics like the above can be formed also by exposing active light still more preferably.

[0056]

[Working example]Next, the embodiment of this invention is shown. This invention is not limited by the embodiment shown here. The "part" in an embodiment and a comparative example shows a weight section.

[0057]synthetic example 1A ethylene-glycol-monomethyl-ether 95 copy toluene 45 copy B AMP-60G (the Shin-Nakamura Chemical Co., Ltd. make.) trade name type (I) of phenoxy polyethylene glycol acrylate -- n=6 30 copy Benzyl methacrylate 30 copy ethylene-glycol-monomethyl-ether methacrylic acid 40-copy 2,2'-azobis (isobutyronitrile) 1 copy C. 10 copy hydroquinone 0.05 copy D Glycidyl methacrylate 33 copies Bird methylbenzyl ammoniumchloride 0.1 copy Ethylene glycol monomethyl ether 38 copies Toluene 12 copies[0058]The above-mentioned B was uniformly dropped over 3 hours, having carried out temperature rising of the above-mentioned A to 78 °C under a nitrogen gas atmosphere in addition to the reactor with a volume of about 500 ml in which heating and cooling are possible with a thermometer, an agitating device, a condenser tube, a gas introducing pipe, and a dropping machine, and keeping reaction temperature at 78 °C. After dropping of B, and after continuing churning at 78 °C for about 6 hours, the above-mentioned C was added and churning was continued for 15 minutes. The above-mentioned D was uniformly dropped over 1 hour, having continued, having changed the inside of a reactor to the atmosphere of dry air, having carried out temperature rising of the temperature to 100 °C, and keeping reaction temperature at 100 °C. Churning was continued at 100 °C after dropping of D for about 20 to 24 hours, and the unsaturated high molecular compound (A-1) of the acid number 118 was obtained (weight per epoxy equivalent / carboxyl equivalent ratio =0.4).

[0059]The unsaturated high molecular compound (A-2) of the acid number 115 was obtained by operating AMP-60G like the synthetic example 1 by B of the example 1 of synthetic example 2 synthesis except having changed 20 copies and benzyl methacrylate into 40 copies, and having changed 40 copies and 2,2'-azobis (isobutyronitrile) into one copy for methacrylic acid.

[0060][B of the example 1 of example of comparison synthesis 1 synthesis] [AMP-60G]

[except having changed three copies, 57 copies of benzyl methacrylate, 40 copies of methacrylic acid, and 2,2'-azobis (isobutyronitrile) into one copy] By operating it like the reference example 1, the unsaturated linear macromolecule compound (A-3) of the acid number 116 of the system of reaction was obtained.

[0061]synthetic example 3A EPPN-201 (the Nippon Kayaku Co., Ltd. make.) 741 copies of phenol novolak type epoxy resin Propylene-glycol-monomethyl-ether acetate 800-copy B acrylic acid 285 copies Paraben ZOKINON 7.1 copies Benzyltrimethylammonium chloride salt 1.25 copy C tetrahydro phthalic anhydride 234 copies[0062]B was uniformly dropped over 0.5 hour, having carried out temperature rising of the above-mentioned A to 115 °C in addition to the reactor with a volume of about 5 l. in which heating and cooling are possible with a thermometer, an agitating device, a condenser tube, a dry air introducing pipe, and a dropping machine, and keeping reaction temperature at 110-120 °C. After dropping of B, and after continuing churning at 115 °C for about 20 hours and making the acid number of the system of reaction or less into 13, it cooled at 65 °C and C was added. The after-addition system of reaction of C was kept at 65 °C, churning was continued for about 6 hours, and the tetrahydro phthalic anhydride denaturation epoxy acrylate of the acid number 84 was obtained (acid equivalent/weight per epoxy equivalent =1.01).

[0063]The (A) component obtained in Embodiments 1-7, the comparative example 1 - the examples 1-2 of 4 synthesis, and the example 1 of comparison synthesis and the (B) component obtained by the reference example 3, the (C) component, the (D) component, the color, and the organic solvent were mixed by the blending ratio (weight section) shown in the following and Table 1, respectively, and the solution of the photosensitive resin composition was obtained. Next, the solution 6 of the photosensitive resin composition of the above-mentioned combination was uniformly applied on the 25-micrometer polyethylene terephthalate film 12 of thickness using the device shown by [drawing 1](#), and it dried for about 10 minutes with the 80-100 °C hot blast convection type dryer 7. The thickness after desiccation of the layer of a photosensitive resin composition was about 35 micrometers. On the layer of a photosensitive resin composition, as it was further shown in [drawing 1](#), the polyethylene film 13 about 25 micrometers thick was pasted together as a cover film, and the photosensitive element was obtained. As for a knife and 8, in Fig. 1, a polyethylene terephthalate film delivery roll, and 2, 3 and 4 are [a roll and 11] photosensitive element winding rolls a polyethylene film delivery roll, and 9 and 10 a roll and 5 1.

[0064]

[Table 1]

	配 合	配合量
(A)	合成例1～2及び比較合成例1で得られた不飽和線状高分子化合物	(表2参照)
(B)	合成例3で得られたテトラヒドロ無水フタル酸変性エポキシアクリレート	(表2参照)
(C)	BPE-10 (新中村化学工業株式会社製、ビスフェノールAポリオキシエチレンジメタクリレートの商品名)	(表2参照)
(D)	I-651 (チバ・ガイギー株式会社製、ベンジルジメチルケタールの商品名)	6.0部
	・ピクトリアピュアブルー (染料)	0.04部
	・メチルエチルケトン (溶剤)	20部

[0065]It examined [photosensitive element / which was obtained] by the following methods about the development nature to an alkaline aqueous solution, exposure sensitivity, spilling nature, preservation stability, and the non-[proof] electrolytic copper metal-plating nature after resist formation. The result was shown in Table 1.

[0066](1) Substrate ACL-E-168 [to an alkaline aqueous solution] for additive processes by development nature Hitachi Chemical Co., Ltd. () [both sides of Pd system metal-plating catalyst content glass epoxy laminated sheet] the substrate which applied the phenol denaturation nitrile rubber adhesive containing a metal-plating catalyst to a thickness of about 30 micrometers -- the Sumitomo 3M Scotch whisky -- it was bright, ground, washed and dried at 80 ** for 15 minutes. The photosensitive element obtained above by both sides of this examination board was laminated stripping the cover film of polyethylene using the product A-500 type laminater made from Dawn Industry. Next, after stripping a polyethylene terephthalate film, spray development was carried out for 30 seconds at 30 ** using the sodium carbonate aqueous solution 1weight %. Viewing estimated after development the resin which is expanded by 30 times and remains. dealing in the basis of evaluation with that of the following -- it is .

O: good thing (that by which resin does not remain at all on substrate face) of development nature
x: The poor thing of development nature (that by which resin remains for a while on a substrate face)

[0067](2) After laminating a photosensitive element to an examination board like exposure sensitivity (1), Kodak step tablet No.2 (the Eastman Kodak Co. make.) The 21-step step tablet was stuck to the photosensitive layer from on the polyethylene terephthalate film, the Oak Work Place HMW-590 type exposure machine was used, and the light exposure (mJ/cm²) required in

order to obtain seven steps of step tablet numbers of stages was calculated.

[0068](3) After keeping a spilling sexual feeling photic element at the temperature of 23 **, and 60% of humidity for 24 hours, the polyethylene cover film was stripped, the cutter knife cut at fixed velocity, and viewing estimated the state of spilling of the photosensitive layer of a cut section. dealing in a valuation basis with that of the following -- it is .

O: what has good spilling nature (thing without KAKE of photosensitive layer)

**: What has a little poor spilling nature (what has KAKE of a photosensitive layer a little)

x: What has poor spilling nature (KAKE of a photosensitive layer is a certain thing remarkably)

[0069](4) The photosensitive element with a length of 90 m rolled round in the shape of a preservation stability roll was kept at the temperature of 23 **, and 60% of humidity, and viewing estimated the situation of exudation of the photosensitive layer from the roll side over six months. dealing in a valuation basis with that of the following -- it is .

O: what has good preservation stability (that in which at least six months do not have exudation of photosensitive layer)

x: What has poor preservation stability (what exudation of the photosensitive layer generated in six months)

[0070](5) the examination board which opened a through hole 0.8 mm in diameter in substrate ACL-E-168 for additive processes by Hitachi Chemical Co., Ltd. of the non-[proof] electrolytic copper metal-plating nature above-mentioned at intervals of 2.54 mm with NC drill -- the Sumitomo 3M Scotch whisky -- it being bright, grinding, washing and, Stoving was carried out at 80 ** for 15 minutes. After laminating the photosensitive element obtained by both sides of this examination board, removing a polyethylene cover film using the product A-500 type laminater made from Dawn Industry, The negative mask for an examination shown in drawing 2 was stuck from the polyethylene terephthalate film, and the Oak Work Place HMW-590 type exposure machine was used, and it exposed so that seven steps of step tablet numbers of stages might be obtained. After exposure, the negative mask was heated for 5 minutes at 80 **, after exfoliating. In drawing 2, 14 shows the opaque portion of a negative mask and 15 shows the transparent area of a negative mask.

[0071]Next, spray development was carried out for 70 seconds at 30 ** using the sodium carbonate aqueous solution 1weight %. Stoving was carried out for 10 minutes at 80 ** after development, and it re-irradiated with ultraviolet radiation in the quantity of 3 J/cm² using the black light by Toshiba Electric Equipment Corp. It heated at 150 ** for 1 hour. Thus, the examination board in which the resist image was formed was immersed in the 40 ** solution which melted the sodium dichromate 20g in 42% of fluoroboric acid aqueous solutions [1 l. of] for 15 minutes, and the exposed portion of the adhesive layer was roughened, and it was immersed in hydrochloric acid with a concentration of 3 N for 5 minutes after the flush, and washed. This examination board CuSO₄ and 5H₂O15 g/l, 30 g/l of ethylenediaminetetraacetic acid, It was immersed in the non-electrolytic copper plating solution prepared to pH 12.5 by

sodium hydroxide including HCHO aqueous solution 10 ml/l and sodium cyanide 25 mg/l 37% at 72 ** for 24 hours, and dried for 10 minutes at 80 ** after the flush.

[0072]After performing such operation, the resist image was expanded by 30 times and viewing estimated the situation of the crack generation of a resist, and the float from a substrate and the existence of peeling, dealing in a valuation basis with that of the following -- it is .

O: what has good non-[proof] electrolytic copper metal-plating nature (what does not have development of crack, float, and separation in resist)

** : What has a little poor non-[proof] electrolytic copper metal-plating nature (what floated in a part of resist and separation generated)

x: What has poor non-[proof] electrolytic copper metal-plating nature (what a crack, a float, and separation generated all over the resist)

[0073]

[Table 2]

表 2

実施例 5	実施例 6	実施例 7	比較例 1	比較例 2	比較例 3	比較例 4
50	—	—	10	—	—	—
—	40	50	—	—	—	—
—	—	—	—	30	40	50
25	50	25	80	60	45	25
25	15	25	10	10	15	25
○	○	○	○	○	○	○
200	200	150	200	200	150	200
○	○	○	x	x	x	△
○	○	○	x	○	○	○
○	○	○	x	△	x	x

数を示す。

項 目		実施例 1	実施例 2	実施例 3	実施例 4
(A)成分 (部)	A-1	30	40	40	—
	A-2	—	—	—	30
	A-3	—	—	—	—
(B)成分 (部)	(部)	60	50	45	60
(C)成分 (部)	(部)	10	10	15	10
アルカリ現像性		○	○	○	○
露光感度 (mJ/cm ²)		200	200	200	250
飛び散り性		○	○	○	○
保存安定性		○	○	○	○
無電解銅めっき性		○	○	○	○

(A)、(B)及び(C)成分の部数は、固形分の部数

[0074]
[Effect of the Invention][the photosensitive element obtained using the photosensitive resin composition and this which become this invention] Since the metal-plating resist which shows good alkali development property, and is excellent in sensitivity and resolution, and is formed of these has neither the abnormal precipitation of metal-plating copper, nor contamination of a plating solution and is excellent in metal-plating-proof nature, it is preferred as a metal-plating resist for non-electrolytic copper metal plating. Since the photosensitive element which becomes this invention is excellent in workability since spilling does not occur at the time of cutting, and it is excellent also in preservation stability, its yield of manufacture of a printed wiring board etc. can also improve.

[Brief Description of the Drawings]
[Drawing 1]The schematic illustration of the manufacturing installation of a photosensitive element used by the embodiment and the comparative example

[Drawing 2] The figure showing the negative mask for an examination used by the embodiment

and the comparative example

[Explanations of letters or numerals]

1 -- Polyethylene terephthalate film delivery roll

2, 3, 4 -- Roll

5 -- Knife

6 -- Solution of a photosensitive resin composition

7 -- Dryer

8 -- Polyethylene film delivery roll

9, 10 -- Roll

11 -- Photosensitive element winding roll

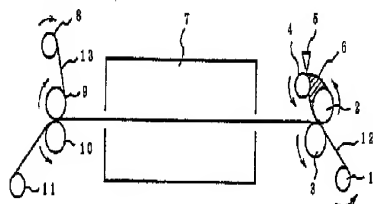
12 -- Polyethylene terephthalate film

13 -- Polyethylene film

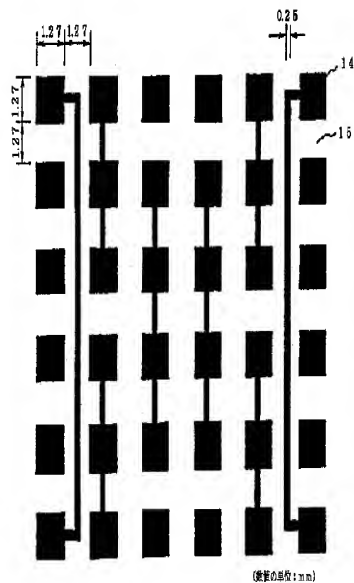
14 -- Opaque portion of a negative mask

15 -- Transparent area of a negative mask

[Drawing 1]



[Drawing 2]



[Translation done.]

Report Mistranslation

Japanese (whole document in PDF)